



# Cyclobutadiene rhodium complexes as catalysts for the synthesis of amides from electron-rich arenes, tosyl azide and CO

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Dedicated to Professor Elena S. Shubina in recognition of her outstanding studies of organometallic compounds by IR spectroscopy and on the occasion of her anniversary.

# Abstract

Cyclobutadiene rhodium complexes [( $C_4R_4$ )RhX]<sub>2</sub> (R=Et, Ph; X = I, Cl) at 0.5 mol% loading catalyze the

Introduction
Diene rhodium complexes are readily available<sup>[1]</sup> from RhCl<sub>3</sub> and are widely used as catalysts for various organic transformations.<sup>[2-4]</sup> However, in most cases the labile diene ligands are replaced at the first step of the catalytic cycle to give some other active species. Recently, we have developed a general appress of the catalytic cycle to give some other active species. Recently, we have developed a general appressor to the rhodium complexes with cyclobutadiene ligands.<sup>[5,6]</sup> which bind metals much strong Scheme 1).<sup>[7,8]</sup> Rhodium cyclobutadiene complexes proved to be effective cm<sup>4</sup> iazoesters into E-H bonds,<sup>[9]</sup> as well as for reductive aminative resence of CO.<sup>[6,10]</sup> In both reactions the cyclobutad<sup>4</sup>.

Recently, Bao, Gu, Xia et al. have reported a new unusual method for the synthesis of aryl amides from electron-rich arenes, tosyl azide, and CO. [11-13] The described reaction does not require the presence of any directing groups in arene and various functional groups. However, its efficiency is undermined by the use of the large amounts of the diene rhodium catalyst [(cod)RhCl]<sub>2</sub> (10 mol % based on Rh). Therefore, we decided to find out if it is possible to improve the reaction efficiency by using the more robust cyclobutadiene rhodium complexes as catalysts.

# Scheme 1. Hypothesis for investigation of cyclobutadiene complexes as catalysts.



= low catalyst stability

strong Rh-cyclobutadiene bond = more robust catalyst?

## **Results and discussion**

## **Catalytic studies**

We started our investigation with the model reaction of N-methylindole with tosyl azide in MeCN in the presence of 1 atm of CO at 80 °C (Scheme 2, Table 1). The readily available<sup>[6]</sup> complex  $[(C_4Et_4)Rh(xylene)]PF_6$  (**Rh1**) with strongly-bound cyclobutadiene and loosely-bound xylene ligand indeed promoted this reaction at 1 mol% catalyst loading giving the desired amide 1a in 10% yield (entry 1). Treatment of the complex **Rh1** with [Et<sub>3</sub>NBn]Cl led to the displacement of xylene ligand and the formation of the neutral chloride complex  $[(C_4Et_4)RhCl]_2$  (**Rh2**) in almost quantitative yield.<sup>[5]</sup> This dimeric complex is a close analog of the classical catalyst [(cod)RhCl]<sub>2</sub>. Complex Rh2 has 16 valence electrons and vacant coordination sites on rhodium and therefore can be a more active catalyst. Indeed, the chloride complex Rh2 (at 0.5 mol% loading, that is 1 mol% based on rhodium) was notably more active than the xylene complex **Rh1** and gave the product **1a** in 33% yield (entry **2**). Screening of the solvents showed that the yield of **1a** can be increased up to 70% in nitromethane (entries 4–9). Noteworthy, the addition of water retarded the process (entry 4) presumably because of hydrolysis of the intermediately formed TsNCO (see below). Therefore, it was necessary to use dry distilled solvents to achieve good vields. The use of the iodide complex<sup>[9]</sup>  $[(C_4Et_4)RhI]_2$  (**Rh3**) instead of the chloride  $[(C_4Et_4)RhCI]_2$  (**Rh2**) increased the yield of the product up to 80% in 1,2-dichloroethane (entry 10), while in nitromethane the yield dropped to 42% (entry 11). The decrease of the catalyst loading from 0.5 to 0.25 mol% led to the notably lower yield of 59% (entry 13).

We also tested the more bulky tetraphenyl-cyclobutadiene complexes  $[(C_4Ph_4)Rh(xylene)]PF_6$  (**Rh4**) and  $[(C_4Ph_4)RhCl]_2$  (**Rh5**) as catalysts and found that the latter have similar activity to **Rh3** under the standard conditions (entry 16 vs 10). Interestingly, under the increased pressure of CO (40 bar) even very low amounts of the catalyst **Rh5** (0.05 mol%) gave the product **1a** in good yield 62% (entry 16). Finally, we tested the cyclooctadiene complex  $[(cod)RhCl]_2$  as the catalyst under our optimized conditions and unexpectedly found very similar activity (entry 18). Apparently, the strongly coordinating MeCN solvent that has been used previously<sup>[11]</sup> diminished the catalytic activity of this complex.

# Scheme 2. Optimization of catalyst and conditions for the model catalytic reaction.

О.

|    |   |                     | ► NHTs                  |                 |
|----|---|---------------------|-------------------------|-----------------|
|    |   | (1 atm)             |                         |                 |
|    | N [Rh],<br>80   | solvent,<br>°C, 24h | N N                     |                 |
|    |   |                     | 1a                      |                 |
| Nº | Catalyst  | Loading,            | Solvent                 | Yield of        |
|    |   | mol%                |                         | <b>1a</b> , %   |
| 1  | [(C <sub>4</sub> Et <sub>4</sub> )Rh(xylene)]PF <sub>6</sub> ( <b>Rh1</b> ) | 1                   | MeCN                    | 10              |
| 2  | [(C <sub>4</sub> Et <sub>4</sub> )RhCl] <sub>2</sub> ( <b>Rh2</b> )         | 0.5                 | MeCN                    | 33              |
| 3  | [(C <sub>4</sub> Et <sub>4</sub> )RhCl] <sub>2</sub> ( <b>Rh2</b> )         | 0.5                 | MeCN                    | 40 <sup>a</sup> |
| 4  | $[(C_4Et_4)RhCl]_2(Rh2)$  | 0.5                 | MeCN                    | 0               |
|    |   |                     | +5 eq. H <sub>2</sub> O |                 |
| 5  | $[(C_4Et_4)RhCl]_2(Rh2)$  | 0.5                 | DCM                     | 19 <sup>b</sup> |
| 6  | $[(C_4Et_4)RhCl]_2(Rh2)$  | 0.5                 | Acetone                 | 15              |
| 7  | $[(C_4Et_4)RhCl]_2(Rh2)$  | 0.5                 | DMF                     | 33              |
| 8  | $[(C_4Et_4)RhCl]_2(Rh2)$  | 0.5                 | DCE                     | 38              |
| 9  | $[(C_4Et_4)RhCl]_2(Rh2)$  | 0.5                 | MeNO <sub>2</sub>       | 70              |
| 10 | [(C <sub>4</sub> Et <sub>4</sub> )RhI] <sub>2</sub> ( <b>Rh3</b> )          | 0.5                 | DCE                     | 80              |
| 11 | [(C <sub>4</sub> Et <sub>4</sub> )RhI] <sub>2</sub> ( <b>Rh3</b> )          | 0.5                 | MeNO <sub>2</sub>       | 42              |
| 12 | [(C <sub>4</sub> Et <sub>4</sub> )RhI] <sub>2</sub> ( <b>Rh3</b> )          | 0.5                 | THF                     | 24              |
| 13 | [(C <sub>4</sub> Et <sub>4</sub> )RhI] <sub>2</sub> ( <b>Rh3</b> )          | 0.25                | DCE                     | 59              |
| 14 | [(C <sub>4</sub> Ph <sub>4</sub> )Rh(xylene)]PF <sub>6</sub> ( <b>Rh4</b> ) | 1                   | MeCN                    | traces          |
| 15 | [(C <sub>4</sub> Ph <sub>4</sub> )RhCl] <sub>2</sub> ( <b>Rh5</b> )         | 0.5                 | MeCN                    | 24              |
| 16 | [(C <sub>4</sub> Ph <sub>4</sub> )RhCl] <sub>2</sub> ( <b>Rh5</b> )         | 0.5                 | DCE                     | 80              |
| 17 | [(C <sub>4</sub> Ph <sub>4</sub> )RhCl] <sub>2</sub> ( <b>Rh5</b> )         | 0.05                | DCE                     | 62 <sup>c</sup> |
| 18 | [(cod)RhCl] <sub>2</sub> ( <b>Rh6</b> )                                     | 0.5                 | DCE                     | 79              |

ased on 1,1,2,2b) The cope of

Typical conditions: N-methylindole (0.5 mmol),  $TsN_3$  (0.6 mmol), CO (balloon), catalyst (1 mol% based on Rh), solvent (2 mL), 80 °C, 24 h. The yields were determined by NMR spectroscopy using 1,1,2,2-tetrachloroethane as the internal standard. a) Two equivalents of tosyl azide were used. b) The temperature of the reaction was 55 °C. c) The pressure of CO was 40 bar.

Following our original idea, we chose the catalyst **Rh3** for further studies and investigated the scope of suitable arenes for this reaction (Scheme 3). N-methyl-indoles with substituents in various positions of aromatic ring smoothly reacted with TsN<sub>3</sub> and CO to give the desired amides **1a**–**e** in 76–88% yields. The yields were somewhat lower (45-71%) in the case of derivatives of non-methylated indoles (**1f-1i**), probably because of some side reactions, such as an electrophilic attack of TsNCO intermediate at the nitrogen atom. Interestingly, N-acetyl-indole did not give the corresponding amide product (**1m**) because the electron acceptor acetyl group reduced the nucleophilicity of arene. Otherwise, the nature of the substituents did not significantly affect the outcome of the reaction: the reaction tolerated both donor (alkyl, OMe) and acceptor groups (halogens, COOMe). Mild steric hindrance in 2-phenyl-indole did not prevent the formation of the product **1g**. Other electron-rich arenes such as pyrrole and guaiazulene also reacted with TsN<sub>3</sub> and CO giving the corresponding amides **1j** and **1k**, albeit in lower

yields because of the lower stability of these arenes themselves. On the other hand, less nucleophilic arenes, such as 1,4-dimetoxybenzene, N,N-dimethylaniline, and ferrocene did not produce the expected products **1n–p**.



Scheme 3. The substrate scope of catalytic amidation of heteroarenes with CO and tosyl azide. Reaction conditions: arene (0.5 mmol),  $TsN_3$  (0.6 mmol), CO (1 atm),  $[(C_4Et_4)RhI]_2$  (0.0025 mmol), 1,2-dichloroethane (2 mL), 80 °C, 24 h. Isolated yields are given. a) 2 mol% of the catalyst were used.

Attempts to use benzyl azide, tert-butyldimethylsilyl azide or the combination of *p*-nitrotoluene and  $CO^{[14]}$  as a source of nitrene instead of tosyl azide were unsuccessful. Similarly, the use of ethyl formate as a source of CO was also ineffective. To sum up, the reaction scope, the yields of products, and the limitations of our catalytic system are very similar to those observed previously with the cyclooctadiene rhodium catalyst [(cod)RhCl]<sub>2</sub>.<sup>[11]</sup> Noteworthy, this low loading (0.5 mol%) makes the cyclobutadiene

rhodium complex more active than palladium catalysts,<sup>[13,15]</sup> which are often used in various carbonylation reactions.

Detailed analysis of the substrate scope (Scheme 3) revealed that the outcome of this catalytic reaction is determined by the nucleophilic properties of the arene and correlates with Mayr's nucleophilicity scale.<sup>[16]</sup> In particular, the nucleophilicity parameter (*N*) for N-methyl-indole is 5.8, for the free indole N =5.6, for methyl- and methoxy-substituted indoles N > 6.0, and for halogen-substituted indoles  $N \approx 4.5$ .<sup>[17]</sup> All these arenes reacted with TsN<sub>3</sub> and CO to give the corresponding amides **1a**–**i**. At the same time, no reaction was observed for the arenes with lower nucleophilicity, such as cyano-indole (N = 2.8), Nacetyl-indole (N = 1.7 for the related N-Boc-indole), or 1,4-dimethoxybenzene (N = 2.5 for the related 1,3-isomer). This approach also explains that benzyl azide did not react because the intermediate isocyanate PhCH<sub>2</sub>NCO is significantly less electrophilic than TsNCO (E = -7.7 for TsNCO vs E = -15.4 for PhNCO).<sup>[18]</sup> Based on Mayr's nucleophilicity scale, it can be predicted that other nucleophiles with parameter N > 4 (such as silyl ethers of enols, enamines, *etc.*) can also react with TsN<sub>3</sub> and CO to give the corresponding amides.

The synthesized amides **1a-1i** were moderately soluble in acetone and ethyl acetate and poorly soluble in other common organic solvents ( $Et_2O$ ,  $CH_2Cl_2$ , etc.). This low solubility significantly complicated their isolation because it required large amounts of solvents for column chromatography. Therefore, we developed an alternative and more efficient purification procedure, which avoids chromatography. First, the excess of tosyl azide and admixture of tosylamide were removed by washing with  $Et_2O$ , and then the remaining product was dissolved in acetone and filtered through the short pad of silica gel to remove the residual catalyst. The obtained samples were spectroscopically pure and did not require additional purification in most cases.

## **Reaction mechanism**

In order to clarify the nature of the active species we carried out the model catalytic reaction at 80 °C with 30 mol% loading of the iodide complex **Rh3** and analyzed the resulting organometallic products by IR- and NMR-spectroscopy as well as mass spectrometry. The mass spectrum contained the signals of the starting complex **Rh3**. The <sup>1</sup>H NMR spectrum showed only the signals of the coordinated cyclobutadiene ligand and the IR spectrum did not show the absorption bands of the possible decomposition products  $[(CO)_2RhI]_2$  or  $[(CO)_2RhI_2]^-$  indicating that the cyclobutadiene remained intact during the catalytic cycle. The reaction of [(C4Et4)Rhl]2 (Rh3) with CO at room temperature in the absence of other organic reagents produced an interesting product Rh7 instead of the expected 18electron complex  $(C_4Et_4)Rh(CO)_2I$  (Scheme 4). The NMR spectra of **Rh7** revealed ambiguous picture with only one type of the cyclobutadiene ligand present in the <sup>13</sup>C NMR spectrum but presumably two sets of cyclobutadiene signals in <sup>1</sup>H NMR spectrum. The IR spectrum of **Rh7** contained a single vibration band of CO ligand at 1855 cm<sup>-1</sup> indicating its bridging coordination mode. The elemental analysis and the highresolution mass spectrum suggested that the formula of Rh7 was [(C<sub>4</sub>Et<sub>4</sub>)Rhl]<sub>2</sub>(CO) (higher oligomers were also observed in HRMS). The DFT calculations of the IR spectra for the model compound  $[(C_4Me_4)RhI]_2(CO)$  (IMO, see below) gave a very similar CO vibration frequency of 1869 cm<sup>-1</sup>. Also, the compound with a similar dimeric structure  $[(C_4Et_4)Rhl]_2(CR_2)$  has been previously identified as intermediate for the rhodium catalyzed carbene insertion reactions.<sup>[9]</sup> We were not able to confirm the structure of Rh7 by X-ray diffraction because of its high solubility and low stability. In fact, the formation of Rh7 was reversible and CO ligand dissociated after several days to give back the starting iodide Rh3. Similar instability has been reported for the related rhodium carbonyl complexes with borole ligands.<sup>[19]</sup>



Scheme 4. The reaction of the complex Rh3 with carbon monoxide and the possible structure of Rh7.

The previous works have shown the formation of the aryl amides **1** from indoles,  $TsN_3$ , and CO proceeds in two steps.<sup>[11,13]</sup> The first step is the catalytic reaction of  $TsN_3$  with CO to give the tosyl isocyanate TsNCO.<sup>[15,20]</sup> The second step is the reaction of TsNCO with indoles to give amides, which does not require a catalyst.<sup>[18]</sup> Bao, Gu, and Xia et al. have proposed that the catalytic conversion of  $TsN_3$  into TsNCO occurs via coordination of  $TsN_3$  with  $[Rh(CO)_2CI]$  species and the subsequent dissociation of  $N_2$ with the formation of the rhodium nitrene intermediate  $Cl(OC)_2Rh=NTs$ .<sup>[11]</sup> The calculated barrier for the formation of the rhodium nitrene intermediate  $Cl(OC)_2Rh=NTs$  from  $[Rh(CO)_2CI]$  species is 29 kcal mol<sup>-1</sup>, suggesting that the reaction can proceed with a reasonable speed at 80 °C in accordance with experimental observations. However, according to our calculations, the formation of the starting species  $[Rh(CO)_2CI]$  from the stable dimer  $[Rh(CO)_2CI]_2$  is unfavorable for enormous 79 kcal mol<sup>-1</sup>,<sup>[21]</sup> which is not surprising for the highly unsaturated 14-electron species with acceptor CO ligands. The proposed nitrene intermediate  $Cl(OC)_2Rh=NTs$  has similarly low stability relative to the starting dimer  $[Rh(CO)_2CI]_2$ . Therefore, we think that the formation of TsNCO from TsN<sub>3</sub> in the presence of  $[(cod)RhCI]_2$  or  $[Rh(CO)_2CI]_2$  catalysts proceeds via some other mechanism, possibly via dimeric complexes or via cycloaddition of TsN<sub>3</sub> as described below for the cyclobutadiene rhodium complexes.

We calculated a possible mechanism for the model reaction of  $[(C_4Me_4)RhI]_2$  catalyst with TsN<sub>3</sub> and CO at PBE/3ζ level (Figure 1).<sup>[22]</sup> The initial addition of CO is favorable for 16.1 kcal mol<sup>-1</sup> and leads the dimeric complex with a bridging carbonyl ligand **IMO**. The structure of **IMO** is similar to that proposed for the experimentally obtained complex **Rh7**. Addition of the second CO molecule leads to the cleavage of dimeric structure and gives the unsaturated 16-electron monomeric species [(C<sub>4</sub>Me<sub>4</sub>)Rh(CO)I] (**IM1**), which have similar stability to **IMO**. Subsequent coordination of tosyl azide requires ca. 7 kcal mol<sup>-1</sup> because of the very small enthalpy gain and the unfavorable entropy contribution. Note that the rhodium atom can coordinate either with the substituted nitrogen atom of TsN<sub>3</sub> (**IM2a**) or with the terminal one (**IM2b**) and these intermediates have similar stability. The azide complex **IM2a** can then split off a nitrogen molecule via the transition state **TS1a** to form the nitrene complex **IM3a**, but the activation barrier for this process is rather high  $\Delta G^{\dagger} = 30.2$  kcal mol<sup>-1</sup>. Subsequent addition of CO to the coordinated nitrene proceeds much easier via **TS2a** ( $\Delta G^{\dagger} = 19.9$  kcal mol<sup>-1</sup> from **IM3a**) to give loosely-bound isocyanate complex [(C<sub>4</sub>Me<sub>4</sub>)Rh(CO)(TsNCO)I], which dissociates into the catalytically active species **IM1** and the product TsNCO. The overall formation of TsNCO and N<sub>2</sub> from TsN<sub>3</sub> and CO is energetically favorable for 64.6 kcal mol<sup>-1</sup>.

Figure 1. Calculated standard Gibbs free energies (at PBE/3 $\zeta$  level) for the possible mechanisms of the conversion of TsN<sub>3</sub> and CO into TsNCO and N<sub>2</sub> in the presence of the cyclobutadiene rhodium complexes. Energies are given in kcal mol<sup>-1</sup> relative to the presumed active species [(C<sub>4</sub>Me<sub>4</sub>)RhI(CO)] (IM1).



The mechanisms involving coordinated nitrenes are often assumed in the literature. Interestingly, we found another possible pathway for the transformation of  $TsN_3$  into TsNCO, which is more energetically favorable (Figure 1). In this case the key step is the intramolecular nucleophilic attack of azide on CO ligand in the intermediate **IM2b**, which proceeds via **TS1b** with activation barrier  $G^{\dagger} = 21.7$  kcal mol<sup>-1</sup> and gives the metallacycle intermediate **IM3b**. Despite looking exotic, similar metallacycles have been isolated previously from the reaction of the carbonyl molybdenum complexes with organic azides<sup>[23]</sup> and have been shown to act as the intermediates for the formation of isocyanates.<sup>[24]</sup> In our case, however,

the metallacycle **IM3b** is rather unstable and its retro-cycloaddition has a low barrier ( $\Delta G^{\dagger} = 3.6$  kcal mol<sup>-1</sup> from **IM3b**). As a result, **IM3b** directly gives the product TsNCO as well as the labile nitrogen complex [( $C_4Me_4$ )Rh(N)\_2I], which easily exchanges N<sub>2</sub> for CO to regenerate the catalytically active species **IM1**. Similar mechanism has been recently proposed and calculated for the palladium-catalyzed reactions.<sup>[25,26]</sup> The important conclusion from this pathway is that reactions of TsN<sub>3</sub> in the presence of the transition metal catalysts may proceed without the intermediate formation of the commonly assumed nitrene complexes. This hypothesis also provides a possible explains for the absence of by-products of the direct nitrene insertion into C–H bond of indoles in our case. The overall proposed mechanism for the amidation of indoles is given on Scheme 5.





# Conclusions

We have shown that cyclobutadiene rhodium complexes are the active catalysts for the reaction of donor arenes with tosyl azide and CO. The range of substrates for this class of transformations is determined by the nucleophilic and electrophilic properties of the reagents and can be predicted by Mayr's nucleophilicity scales. According to DFT calculations the reaction is likely proceed via cycloaddition mechanism which does not include the formation of nitrene intermediates.

# Acknowledgments

The main synthetic work was supported by the Russian Science Foundation (grant # 19-73-00278). Access to the electronic resources and databases was provided by INEOS RAS with financial support from the Ministry of Science and Higher Education of the Russian Federation.

**Keywords:** Carbonyl ligands, Cyclobutadiene, Density functional calculations, Homogeneous catalysis, Rhodium.

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#### **Table of contents**



**Catalysts of a new type:** Readily available cyclobutadiene rhodium complexes catalyze the synthesis of amides directly from donor arenes, CO, and tosyl azide. The scope of substrates for such transformations can be rationalized in terms of nucleophilic and electrophilic properties of reagents.